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BONDING PROBLEMS IN MAIN GROUP CHEMISTRY

Karl Christe,[a,b] David Dixon,[c] Jerry Boatz[a]

[a]Air Force Research Laboratory, Edwards AFB,
[b]University of Southern California,
[c]Pacific Northwest National Laboratory

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Background

- Not a theoretician, but simple-minded experimentalist who takes advantage of synergism between theory and synthesis

- Main interests: Synthesis and characterization of novel challenging compounds,
  Nature of bonding,
  Strength of bonds,
  Barriers towards decomposition

- Enormous progress has been made in stability and barrier calculations, but a good general understanding of bonding is still frequently lacking. Even for simple compounds such as SF_6, there is no consensus on the nature of the bonding (participation of *d*-orbitals), and, for the most part, the "modern aspects" are not so modern.

- Caveat: Descriptions of bonding are only attempts to interpret in an oversimplified manner complex problems which are not accessible to direct measurements, and our descriptions of bonding represent only our best understanding at a given time and these descriptions also change with time.

Overview of some of the problems encountered in our work

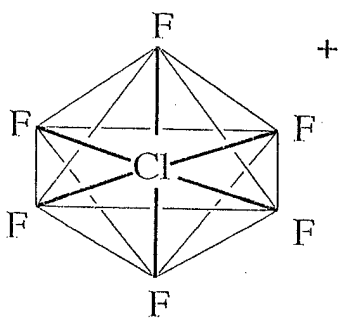
- Role of semi-ionic, multi-center bonding in complex fluoride and oxofluoride chemistry
- Steric activity of free valence electron pairs
- How does the replacement of fluorine ligands in pentagonal-bipyramidal or octahedral compounds by doubly bonded oxygen or free valence electron pairs influence the bonding ?
- Stability predictions for FN_5, $N_5^+N_3^-$ and $N_5^+N_5^-$
- Are covalent azides with linear M-N-N bonds for real ?

Role of semi-ionic , multi-center bonding

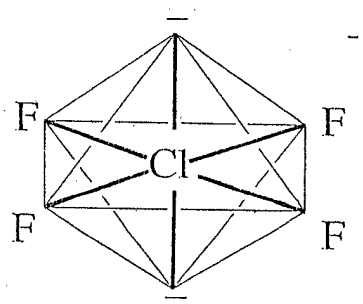
- In 1963, we became interested in halogen fluoride chemistry and since then have prepared and characterized many new main group compounds.

- Relied heavily on vibrational spectroscopy and normal coordinate analyses for the characterization (work done mainly with W. Sawodny and E. Curtis).

- Found huge differences in the valence force constants between different and even within the same compounds that could not be explained by repulsion arguments (VSEPR) alone.



$f_r = 4.7$ mdyn/Å



fr = 2.1 mdyn/Å

Role of semi-ionic , multi-center bonding

- The following empirical rules were developed by us over the years to explain our experimental observations:
  - The bonding in main group halides and oxohalides involves predominantly the *s*- and *p*-orbitals of the central atom giving rise to the orthogonality of the bonds.
  - Sterically active free valence electron pairs on the central atom or doubly bonded oxygen ligands seek as much *s*-character as possible by forming mainly covalent bonds involving sp_n hybrids.
  - The remaining halogen ligands form highly ionic, multi-center bonds involving the remaining *p*-orbitals of the central atom.

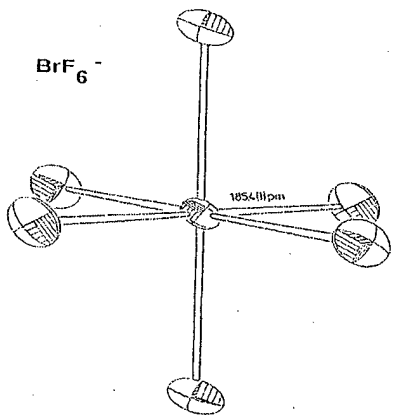
Some commentary about these rules

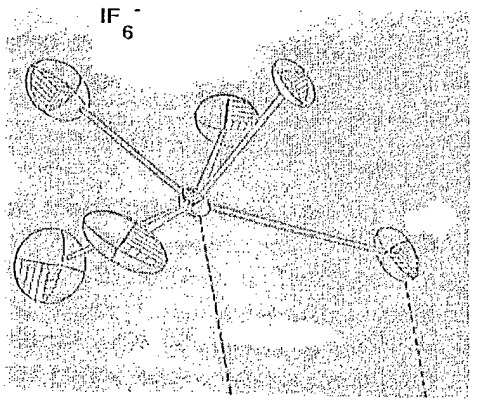
- No black and white situation. Degree of highly ionic, multi-center bonding can vary from compound to compound.
- Secondary effects, such as formal negative or positive charges, oxidation state of the central atom, and electronegativity differences between the central atom and the ligands, can enhance or decrease the contributions from the ionic bonding.
- These rules have held up very well over the years, but have neither been widely accepted nor supported by a systematic theoretical framework.
- They provide a picture of the bonding that is more comprehensive and quantitative than that based on simple VSEPR repulsion arguments. For example, they explain the preference of main group elements for pentagonal-bipyramidal structures with minimal equatorial puckering in the case of coordination number 7.

Steric activity of free valence electron pairs

- Free valence electron pairs of the central atom can become sterically inactive when the maximum coordination number of the central atom is exceeded.

- Typical examples are the IF_6^-, BrF_6^-, ClF_6^- anions which have a free valence electron pair on the central atom. In IF_6^-, the free pair is sterically active and the structure is strongly distorted from O_h, while BrF_6^- and ClF_6^- are perfectly octahedral with the free pairs occupying *s*-orbitals (Bougon, Christe, Seppelt).



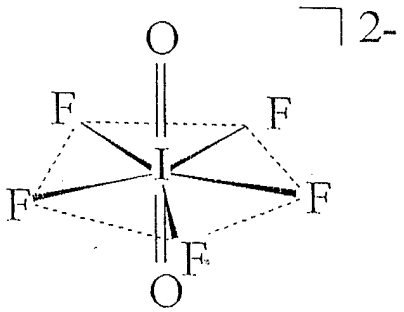


Steric activity of free valence electron pairs

- The steric activity of free pairs is difficult to model in these borderline cases. Theoretical calculations tend to overestimate the space requirements of the ligands and, even for IF_6^-, predict an octahedral structure.
- This problem presents a challenge for the theoreticians to provide better models for the accurate prediction of the sizes of ligands and the steric activity of free valence electron pairs.

Systematic study of the influence of oxygen substitution on bonding in CN 6 and 7

Jerry A. Boatz, Karl O. Christe,* David A. Dixon, Barbara A. Fir, Michael Gerken, Robert Z. Gnann, Hélène P. A. Mercier, and Gary J. Schrobilgen*
(Inorg. Chem. **2003**, *42*, 5282)



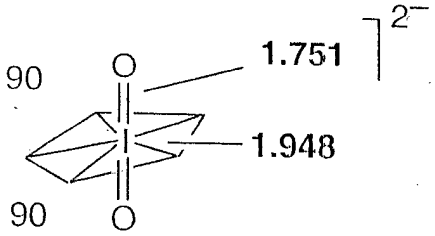
- Synthesized and characterized the novel $IF_5O_2^{2-}$ anion
- First pentagonal-bipyramidal main group AF_5O_2 species and last species that was still missing in AF_5X_2 series of compounds where X = free valence electron pair or doubly bonded oxygen ligand.
- Analysis of the effects of replacing free valence electron pairs by either fluorine or doubly bonded oxygen ligands reveals systematic *trends* that *are dominated by changes in the ionicity of the I-F bonds* due to the formal ionic charges and the oxidation state of the central atom.

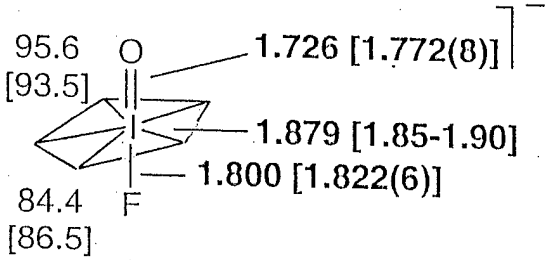
Systematic study of the influence of oxygen substitution and of secondary effects

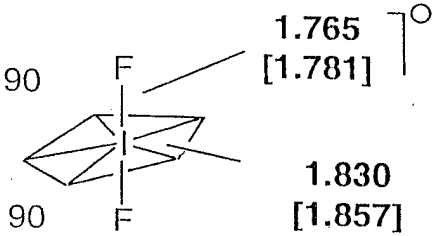
IONIC CHARGE → -2 -1 0

OXID. STATE OF IODINE ↓

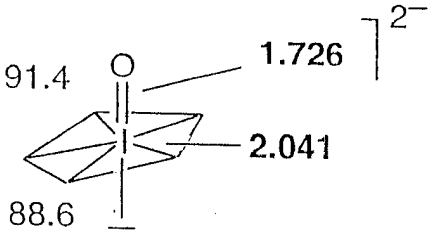
+VII

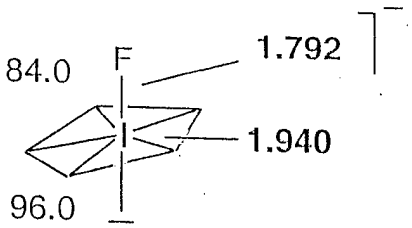




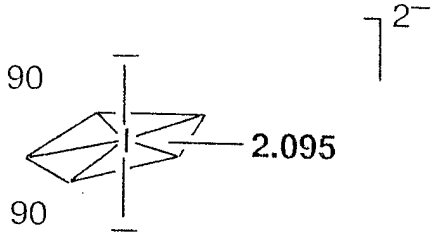


+V





+III



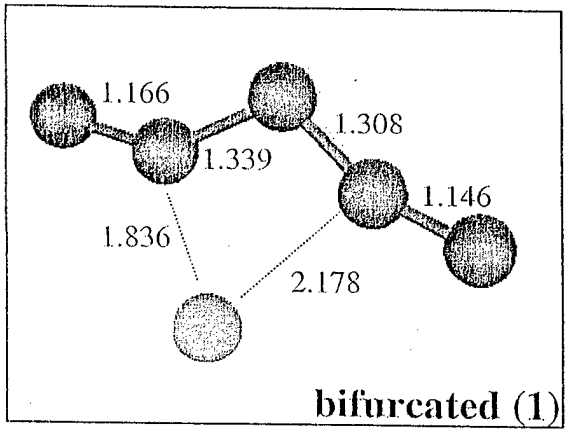
CN 7

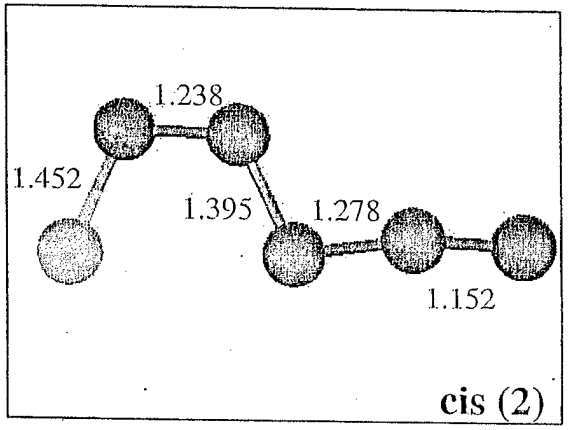
Stability predictions for gases. Example, FN_5

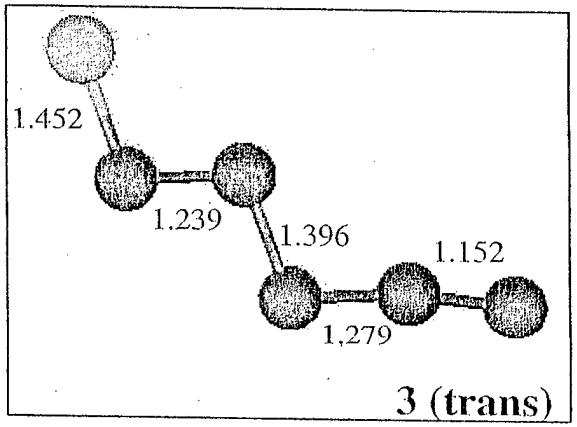
Heather M. Netzloff, Mark S. Gordon, Karl Christe, William W. Wilson, Ashwani Vij, Vandana Vij, and Jerry A. Boatz, *J. Phys. Chem. A,* **2003**, *107*, 6638

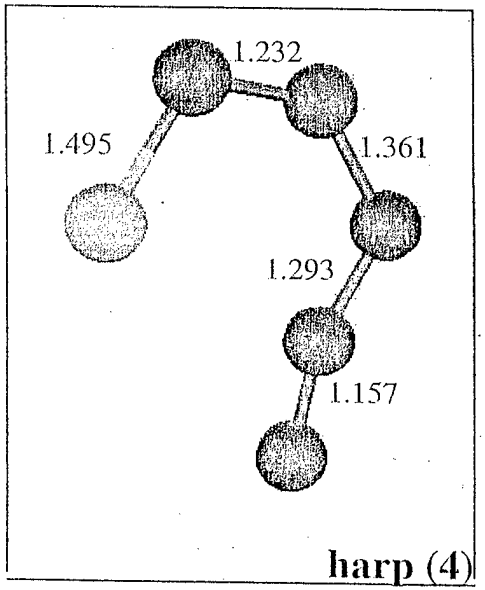
- Controlled decomposition of $(N_5^+)_2SnF_6^{2-}$ to $N_5^+SnF_5^-$ and "FN_5" allowed us to search for FN_5 by dynamic FT-IR spectroscopy
- Observed only FN_3 and its decomposition products (N_2F_2 and NF_3)
- Theoretical study was carried out showing six stable isomers for FN_5 differing only by about 6 (MP2) and 10 (CCSD(T)) kcal/mol in energy
- Intrinsic reaction coordinate and dynamic reaction path calculations were used to study the isomerization and decomposition of FN_5
- Based on a Rice-Ramsperger-Kassel-Marcus analysis, the lifetime of FN_5 was estimated to be in the nanosecond range explaining our failure to observe FN_5 experimentally

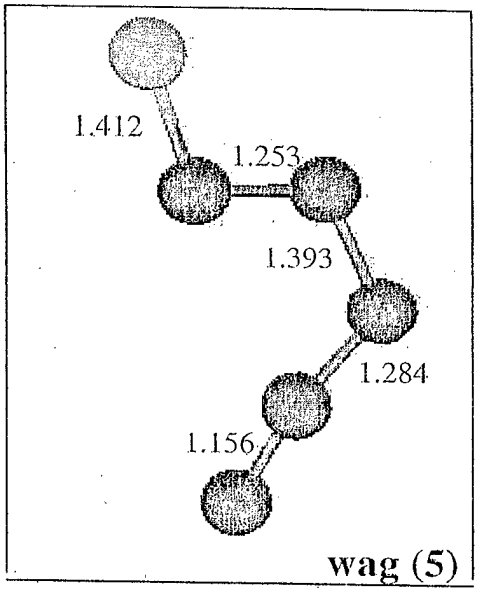
Six FN_5 Isomers (MP2/6-31++G(d,p))

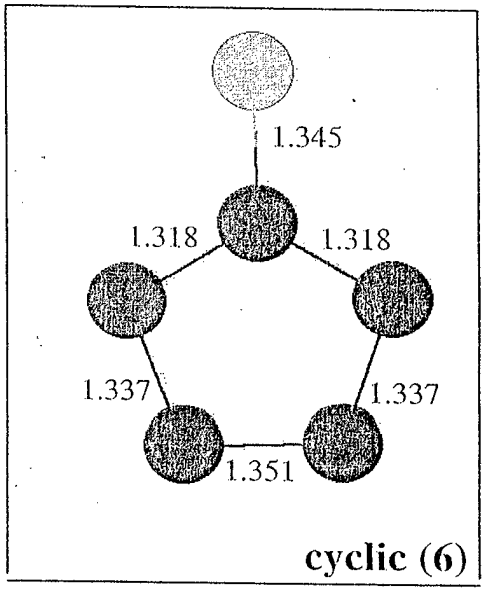




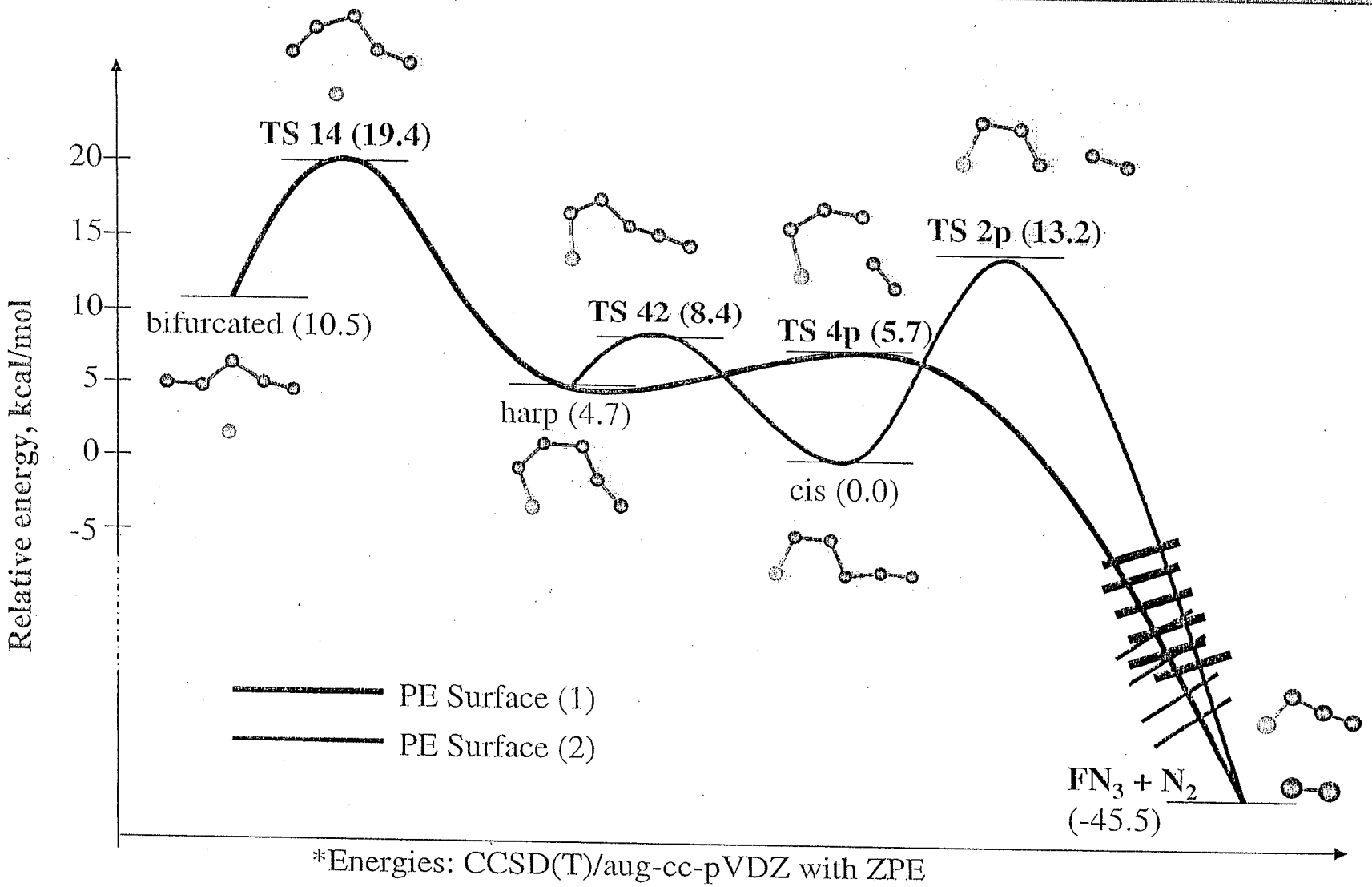








Relative isomerization/decomposition PESs with FN_5 isomers (reference = cis isomer)



*Energies: CCSD(T)/aug-cc-pVDZ with ZPE

Stability predictions for solids $N_5^+N_3^-$ and $N_5^+N_5^-$

David A. Dixon, David Feller, Karl O. Christe, William W. Wilson, Ashwani Vij, Vandana Vij, H. Donald Brooke Jenkins, Ryan M. Olson, and Mark S. Gordon, *J. Amer. Chem. Soc., in press*

- Previously published stability predictions and energy density calculations for $N_5^+N_5^-$ and $N_5^+N_3^-$ are incorrect due to the use of vertical instead of adiabatic electron affinity and ionization potentials, leading to false conclusions.
- The correctness of our theoretical approach was demonstrated by experimentally bracketing the electron affinity of N_5^+ (10.52-11.48 eV) which agrees well with our calculated adiabatic value of 10.55 eV, but not with the vertical value of 6.04 eV.
- Highly accurate enthalpies of formation and adiabatic electron affinities and ionization potentials for N_3, N_3^-, N_5^+ and N_5^- can be calculated from total atomization energies.

Stabilities of $N_5^+N_3^-$ and $N_5^+N_5^-$ from Born-Haber Cycles

$N_5^+N_5^-{}_{(s)} \xrightarrow[-61.4 \pm 5.7]{\Delta H_r} (N_3^{\bullet}{}_{(g)} + N_{2\,(g)}) + (N_3^{\bullet}{}_{(g)} + N_{2\,(g)})$

$\Delta H_L = 134 \pm 5$

$N_5^+(g) + N_5^-(g)$

IP $(N_5^-) = 47.9 \pm 2$

EA $(N_5^+) = -243.3 \pm 2$

- For a salt to be stable, ΔHr must be zero or positive

$N_5^+N_3^-{}_{(s)} \xrightarrow[-36.1 \pm 7.5]{\Delta H_r} N_3^{\bullet}{}_{(g)} + N_3^{\bullet}{}_{(g)} + N_{2\,(g)}$

$\Delta H_L = 146 \pm 7$

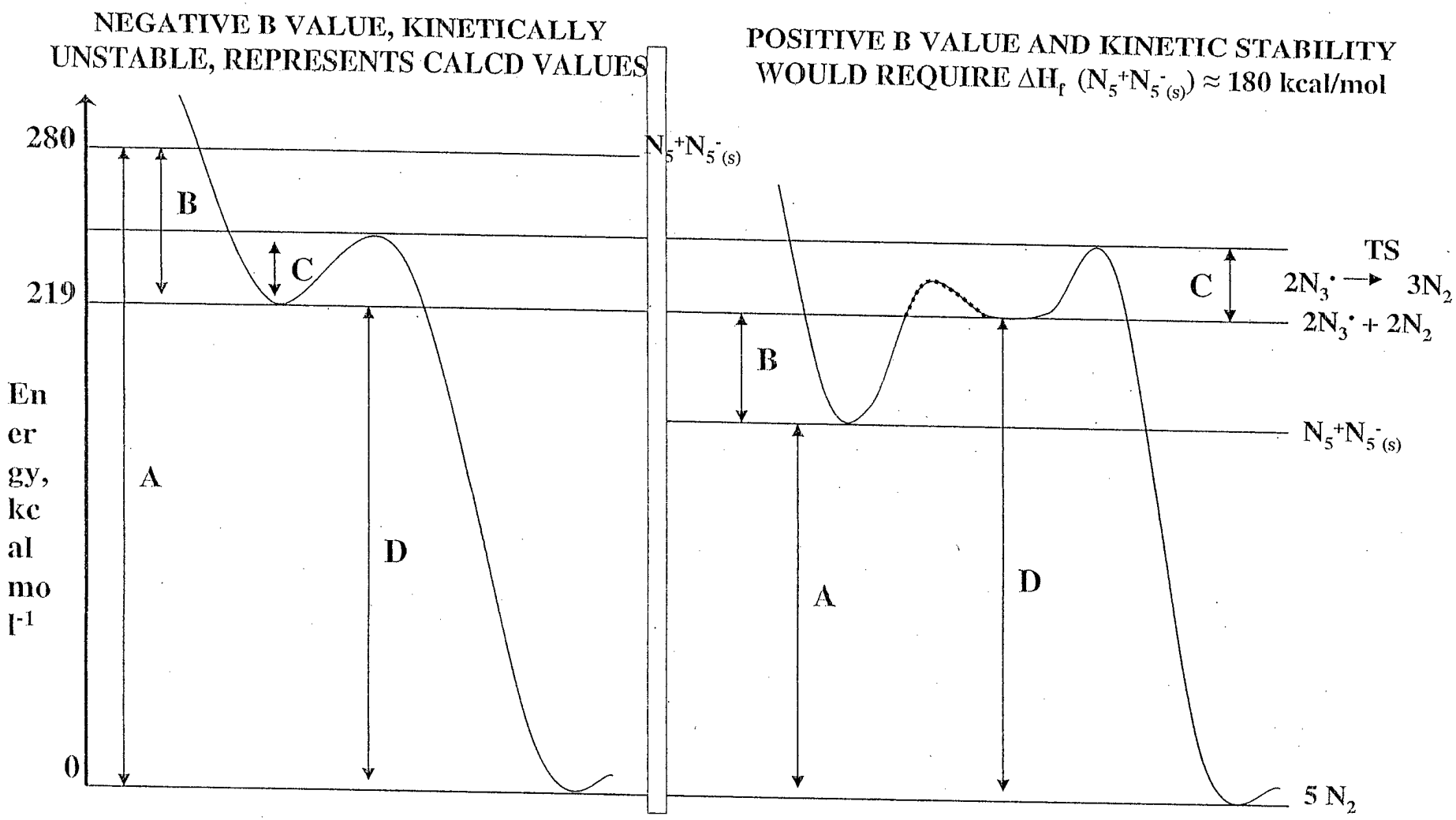
$N_5^+(g) + N_3^-(g)$

IP $(N_3^-) = 61.2 \pm 2$

EA $(N_5^+) = -243.3 \pm 2$

- Problem with the N_5 ions:

Both, cyclic and catenated N_5 radicals are vibrationally unstable and decompose without barrier to N_3. Because N_3 has a barrier, $N_5^+N_3^-$ is less unstable than $N_5^+N_5^-$



A = ΔH_f ($N_5^+N_5^-{}_{(s)}$)

B = ΔH_r ($N_5^+N_5^-{}_{(s)} \longrightarrow$ $(N_5^+{}_{(g)})$ $2N_3^\bullet{}_{(g)} + 2\,N_{2\,(g)}$) = U_L ($N_5^+N_5^-{}_{(s)}$) + 2 RT + IP ($N_5^-{}_{(g)}$) - EA

C = Activation energy barrier for decomposition of $2N_3^\bullet{}_{(g)} \longrightarrow 3N_{2\,(g)}$

D = ΔH_r ($2N_3^\bullet{}_{(g)} \longrightarrow 3N_{2\,(g)}$)

Conclusions concerning the stability of $N_5^+N_5^-$ and $N_5^+N_3^-$

- Our results predict that $N_5^+N_3^-$ and $N_5^+N_5^-$ are unstable and decompose spontaneously with N_2 evolution.

- This conclusion was experimentally confirmed in our laboratory for $N_5^+N_3^-$

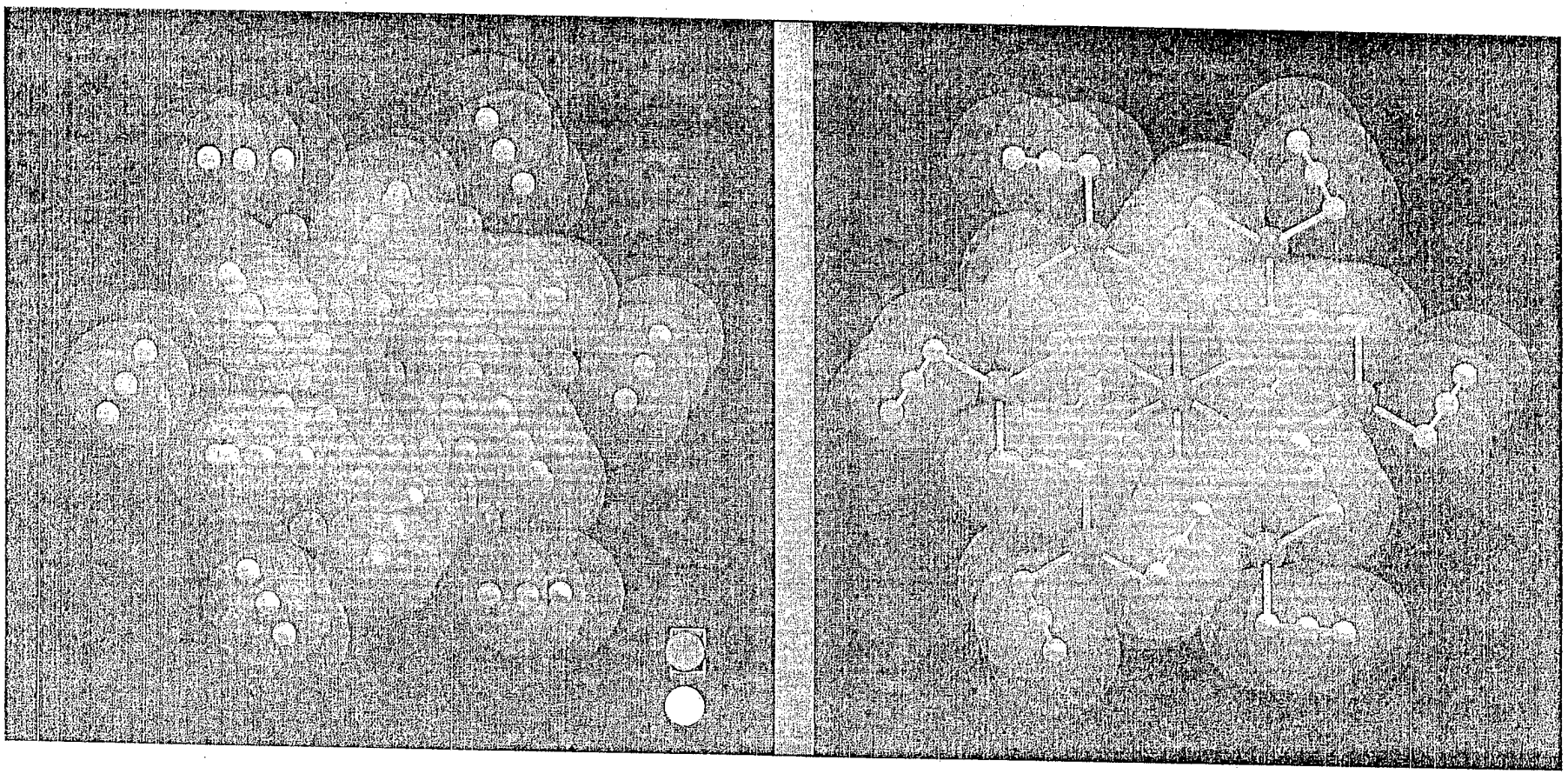
  - Desired metathesis:

$$N_5SbF_6 + CsN_3 \xrightarrow[-64^\circ C]{SO_2} N_5N_3 + CsSbF_6$$

Obtained products:

$$4\ N_2 + CsSbF_6 +$$

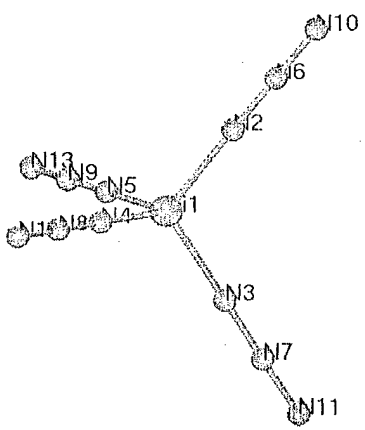
Polyazide Chemistry

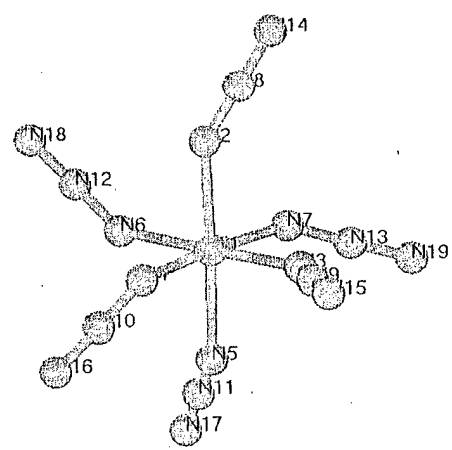


Covalent azides are normally strongly bent with M-N-N angles of about 120 °, as shown here for $Sb(N_3)_3$

Novel type of covalent azides with linear M-N-N bonds

- Based on quantum chemical calculations, Gagliardi and Pyykkoe have recently predicted, (*Inorg. Chem.* **2003**, *42*, 3074), for $Ti(N_3)_4$, $Zr(N_3)_4$, $Hf(N_3)_4$, and $Th(N_3)_4$ a novel type of bonding involving linear M-N-N bonds.
- We have confirmed these calculations for $Ti(N_3)_4$ and also predict that other azides, such as $Fe(N_3)_2$ (Melanie Teichert), can form linear M-N-N bonds. Based on our calculations, we also expect that the $Ti(N_3)_6^{2-}$ anion possesses the usual bent M-N-N bonds.





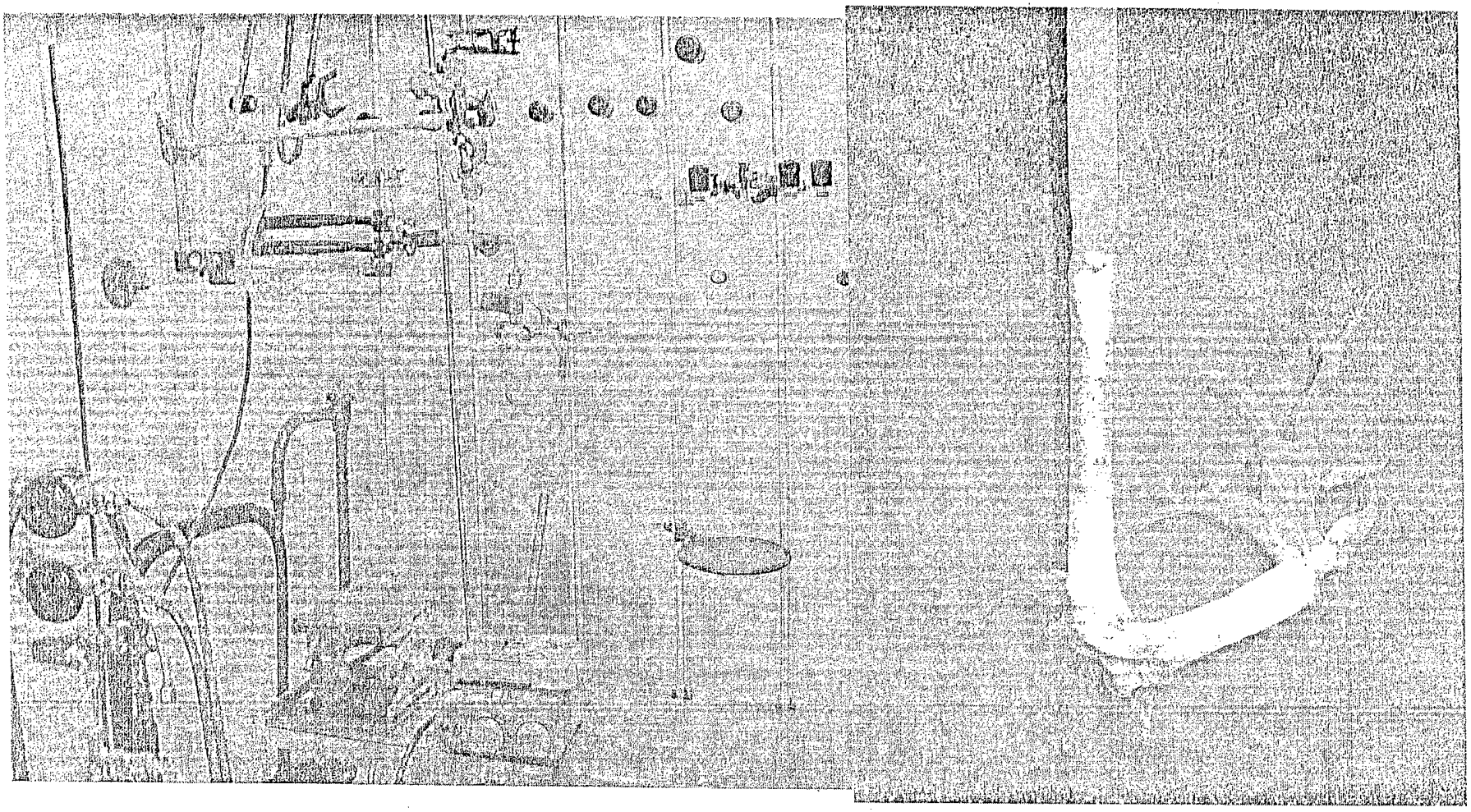
Synthesis and Characterization of $Ti(N_3)_4$

- Ralf Haiges and Jerry Boatz
- Synthesis

$$TiCl_4 + \text{exc. } TMSN_3 \rightarrow Ti(N_3)_4 + 4\ TMSCl$$

- Properties
  - Yellow-orange solid
  - Very shock-sensitive
  - Very low volatility
  - Raman spectrum and comparison with calculated spectra suggest that CN might be higher than 4

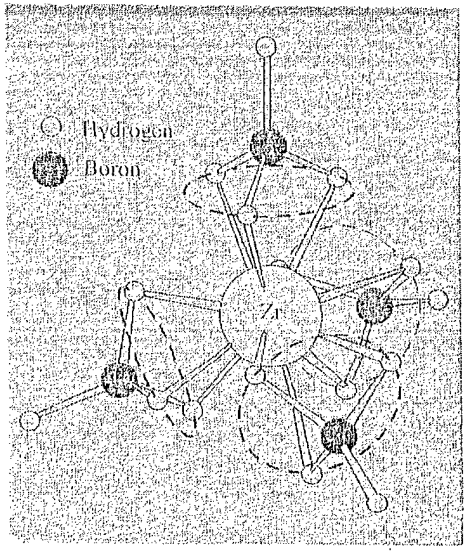
How much damage can ½ mmol of a polyazide cause ?



Possible explanations for linear M-N-N bonds

- Gagliardi and Pyykkoe invoke conjugation.
- We prefer the following interpretation because the calculated Ti-N bond distances are relatively long and are similar to single bonds. Also, the N_β-N_γ bonds are quite short, and the Ti-N-N bonds in $Ti(N_3)_6^{2-}$ are strongly bent.

  ➢ The N_α atom of the $-N_3$ ligand has three free valence electron pairs which can act as a tridentate ligand and, in a tetrahedron, can perfectly overlap with three of the lobes of the Ti 3*d*-orbitals. This scheme is analogous to the structure of $Zr(BH_4)_4$ which possesses 4 trihapto BH_4 groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the N_α atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about 120 °.



Conclusions

- Rapid advances in computer technology have provided great opportunities in computational chemistry.
- Our ability to predict with great precision geometries, stabilities, spectroscopic properties, and decomposition barriers has revolutionized chemistry and provided much insight.
- However, relatively little progress has been made in our fundamental understanding of bonding. Many theoreticians are preoccupied with cranking out numbers while ignoring fundamental concepts.

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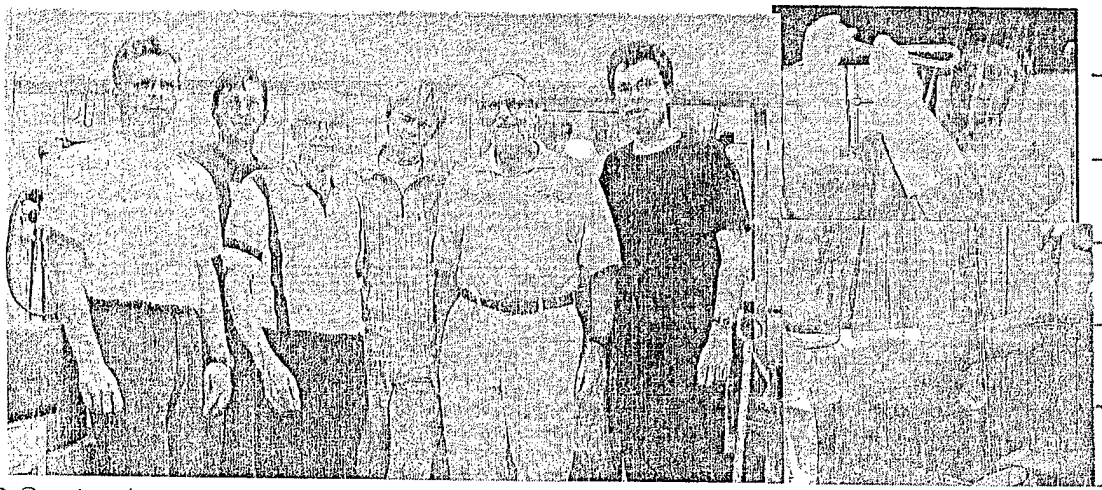
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